DETERMINATION OF THE MICROSTRUCTURE OF WET AND DRY BROWN COAL BY MEANS OF X-RAY SMALL ANGLE SCATTERING

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That brown coal is a highly porous substance and that a knowledge of this pore structure is vital to the efficient and diverse use of brown coal is obvious.

However, what is not so obvious is how to characterize and measure the pore structure of such a heterogeneous material as Victorian brown coal. Even defining what we mean by structure is difficult for such a complex material as coal which contains such diverse constituents as water, carbon, minerals, plant matter, pollen, etc. and whose composition may even vary within a seam. In practice, then, it seems that a Physicist must abandon his usual, precise but simplistic ideas of structure obtained from the study of objects with very regular structures such as crystals and give a description only in terms of such gross parameters as total pore volume, V, total surface area, S, and the distribution of some characteristic dimension, D, of the pores.

There appear to be currently two methods for the determination of the above mentioned parameter.

1) Gas Adsorption (GA) - where the total volume of a gas taken up by the coal is measured and V and S are obtained from this by the use of a model of the adsorption process.

2) Small Angle X-ray Scattering (SAXS) - where the intensity of radiation scattered by the coal is interpreted in terms of the pore structure which causes this scattering.

Both methods are to some extent dependent on models which are used in order to interprete the observed data. No known method can give a very detailed description of the microstructure at this stage. Indeed by the very nature of brown coal such a detailed description is not even, in principle, possible.

However, we will attempt to show that the SAXS method has very many advantages over other methods and we will also show what we have done to date using SAXS.

OUTLINE OF THE TECHNIQUE

Basically x-rays are scattered (just as is light) when a system contains regions which are inhomogeneous over some distance scale, d. These inhomogeneities cause scattering of intensity, I, through various angles, θ. The scattering curve, i.e. intensity as a function of θ or more precisely as a function of

$$h = \frac{2\pi}{\lambda} \sin \frac{\theta}{2}$$

(λ, the X-ray wavelength), contains information about the characteristic dimensions of the inhomogeneities (simplistically h is the reciprocal of d). However, when a wide range of characteristic distances are present the scattering

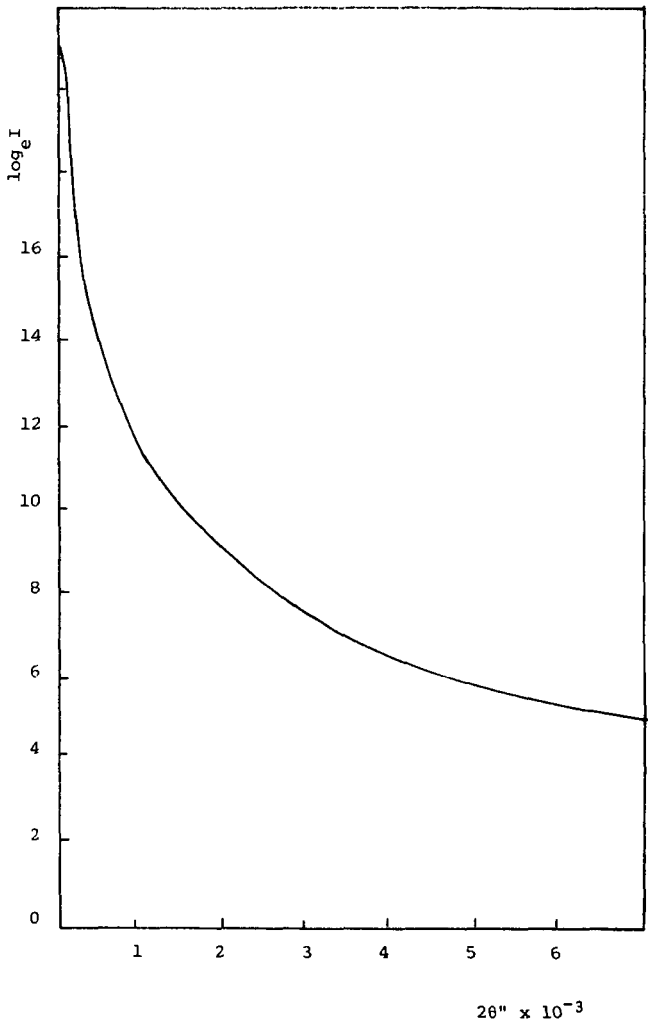

Fig. 1 Scattering curve of air dried coal (light lithotype).

curve is a superposition (convolution) of the effects of all these characteristic distances.

Thus, the scattering curve must be deconvoluted to obtain the information about the spacial distribution of inhomogeneities in the material, e.g. the pore structure in coal.

No known method can do this unambiguously, however, we believe realistic information may be readily and conveniently obtained by this method, e.g. total pore volume.

Furthermore, this method has several advantages over other available methods:

1) the sample can be wet or dry;

2) one can follow various stages of processes involving known coal or even, potentially, follow the material as it goes through these processes e.g. drying;

3) slurries may be studied.

DATA ANALYSIS AND RESULTS

Once the scattering curve has been obtained and stored in some convenient form it must be analysed (deconvoluted) to give details of the pore structure.

Technique to extract the micropore volume and the surface area from the scattering curves has been developed some years ago [1].

All scattering diagrams from brown coals (wet or dry) showed continuous strongly concave curves (Figure 1). This characteristic is assumed to be due to the presence of dilute system of micropores polydisperse in size but approximately identical in shape. From these curves several average pore length parameters can be obtained such as the mean radius of gyration, Rg, calculated by assuming a Maxwellian pore size distribution. Such parameters, although precise do not exactly define the form of the pores, however, can be used to calculate further physical quantities such as the micropore surface area. This quantity was obtained from the combined knowledge of the number of pores in the sample, the micropore volume (both quantities obtained by absolute intensity measurements), the mean radius of gyration, pore shape, and the pore size distribution. The micropore volume is computed directly from the scattering diagram in absolute units. Results are given in Table 1 together with data obtained by means of gas adsorption [2].

For the determination of the surface area we assumed two different shapes for the pores. In (1) we assumed a cylindrical shape and in (2) a disc shape.

Our method of interpretation of the scattering data shows only a partial success as can be seen when the results from the SAXS technique are compared to the results of the GA technique. Theoretically, this method seems to have several major faults:

1a) Assumption, that the pore size distribution is a single mode distribution. Pore size distribution may be more complicated, that is, it may follow a bimodal or even many modal type of distribution function. Indeed this can vary from sample to sample.

1b) Estimation of intensity scattered at zero angle. This point is not reachable experimentally and hence must be estimated, usually by some form of extrapolation. This is a very important quantity since it is directly proportional to the number of micropores within the irradiated volume.

1c) Assumption, that the shape of the micropores is identical. This is only an approximation that significantly simplifies the theoretical equations. It is quite possible that the micropores are not only polydispersed in size but also in shape.

TABLE 1 Comparison of microstructure parameters determined by gas adsorption (GA) and small angle X-ray scattering methods.

LITHOTYPE		MICROPORE VOLUME ml/g		SURFACE AREA m^2/g			RAD. OF GYR. nm
		GA	SAXS	GA	SAXS (1)	SAXS (2)	
DARK	WET	-	0.100	-	30	210	158
	DRY	0.079	0.095	298	90	1100	83
LIGHT	WET		0.110	-	40	390	136
	DRY	0.058	0.060	216	70	830	72

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